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(21) International Application Number: PCT/GB96/02861 (22) International Filing Date: 20 November 1996 (20.11.96) (30) Priority Data: 9523854.9 22 November 1995 (22.11.95) GB (71)(72) Applicants and Inventors: BRATTON, Graham, John [GB/GB]; 154 Old Farm Avenue, Sidcup, Kent DA15 8AL (GB). NAYLOR, Timothy, de Villiers [GB/GB]; Englefield Green, Surrey TW20 0NQ (GB). BUCK, Karon, Doreen [GB/GB]; Alancroft, Kingsfield Road, West Kingsdown, Kent TN15 6LH (GB). (74) Agent: COHEN, Alan, Nicol; 2 Grove Place, Tatsfield, Near Westerham, Kent TN16 2BB (GB).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: WATER REMOVAL DEVICE (57) Abstract A device for removing water from liquid mixtures which comprises a tubular cylinder closed at one end formed from a support matrix on which is crystallised a zeolite membrane over at least its lower part, in use the cylinder is placed in the liquid mixture with the zeolite membrane in contact with the liquid mixture so that the water passes through the membrane into the cylinder, optionally there can be a reduced pressure inside the cylinder.		

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Water Removal Device

The present invention relates to equipment for separating liquids, more particularly it relates to equipment which can be used to separate water from other liquids.

It is known that zeolite membranes can be used to separate water from other liquids and European Patent application 0481660 discloses and discusses prior art zeo-type membranes and refers in particular to US Patents 3244643, 3730910 and 4578372, Applied Catalysts 49(1989) 1-25, DE-A-3827049, CA1235684, JP-A-63287504, JP-A-63291809, EP-A-135069

Conventional use of membranes in liquid separation either involves through-flow methods, where the liquids to be separated are one side of the membrane and by the use of pressure differential or gravity one liquid is passed through the membrane leaving the liquid mixture on the other side of the membrane.

Alternatively, cross-flow separation is used, where the liquid mixture is passed across the surface of the membrane in a continuous or semi-continuous stream and one liquid is removed from the stream by a pressure differential applied across the membrane.

The equipment used in such applications is purpose built and can involve complex pumping and control systems and the liquids are poured into the equipment.

We have devised a simpler and more convenient means of separating liquids which is easier to use in situ.

According to the invention there is provided equipment for separating liquids, which comprises a tubular means which is closed at one end and open at the other and in which part of the tube comprises a zeolite membrane.

The tubular means can be of any cross-sectional shape, e.g. circular, oval, ellipsoidal, rectangular, square, etc., although circular or oval cross-sectional

shapes are preferred. The ratio of length to cross-sectional area of the tubular means is not critical and, depending on its application, a very wide range of shapes can be used, e.g. from long thin tubes to shorter wider tubes.

The part of the tubular means containing a zeolite membrane is preferably a zeolite membrane on a supported matrix such as a metal mesh or sieve, ceramic, a polymer such as a polysulphone or a polyether sulphone etc. as disclosed in the above references. In the present invention the supported membrane can be formed into the desired shape to comprise part of the tubular means.

Preferably the zeolite membrane part of the tubular means is adjacent to the closed end and, if desired, the end can be formed of a zeolite membrane.

The other part of the tubular means can comprise the uncoated membrane support or it can be made of a metal, ceramic, plastic, etc. material. The material is not critical but it should be sufficiently strong enough and dimensionally stable to be suitable. It can be porous or non-porous, depending on how it is to be used.

The zeolite membranes should be substantially free of defects so as to provide an effective separation and zeolite membranes as described in our co-pending application PCT/GB95/02221 in which zeolite membranes are treated with a silicic acid are preferred.

Methods of making silicic acids are described in GB Patent Application 2269377 and a preferred method is by acidification of a sodium silicate solution followed by separation of the silicic acid by phase separation using an organic solvent such as tetrahydrofuran. The organic phase can then be dried and anhydrous silicic acid separated e.g. by addition of n-butanol to obtain a substantially anhydrous solution of silicic acid. The degree of polymerisation of the silicic acid depends on the actual conditions used e.g. the time the sodium silicate solution is in contact with the acid before addition of the organic solvent, temperature etc.

The silicic acid used in the present invention preferably has an average molecular weight in the range of 96 to 10,000 and more preferably of 96 to 3220.

As well as treatment with silicic acids the zeo-type materials can be treated with alkylorthosilicates such as tetra ethyl ortho silicate (TEOS) and tetra isopropyl ortho silicate (TIPO) alkoxyorthosilicates such as tetramethoxyortho silicate which form a polysilicic acid when applied to the zeo-type material. These alkylorthosilicates and alkoxyorthosilicates form mesoporous silica compounds which consist essentially of a series of polysilicic acid units linked together, each unit comprising a polysilicic acid molecule as described in GB Patent Application 2269377 and comprising a plurality of three dimensional species linked together with each species either having silicon atom bridges with an oxygen atom between each silicon atom or hydroxyl groups on the silicon

In one embodiment the tubular means is formed from a matrix which can be used as a support for a zeolite membrane and a zeolite membrane is then deposited, grown, crystallised or formed on part of the support, leaving the other part untreated.

The equipment of the invention can be used in two different ways. In the first way, the device of the invention is placed within a receptacle and the liquid mixture placed within the tubular means so that the liquid mixture is only in contact with the zeolite membrane or non-porous part of the tubular means. The liquid, which can pass through the zeolite membrane, e.g. water, passes through the membrane into the receptacle, thus separating the liquids. A pressure differential is preferably applied across the membrane to facilitate the separation.

In an alternative way of operation, the liquid mixture is contained in a receptacle and the device is placed in the liquid, with a portion of the tubular means comprising the zeolite membrane in contact with the liquid mixture. The liquid, which can pass through the membrane, will then pass into the tubular means and can be removed. A pressure differential can be applied across the membrane to facilitate the separation.

The device is particularly useful in removing water from liquid mixtures containing water, for example, to lower the water content to acceptably low levels, e.g. in solvents, thinners and other liquids which can be contaminated with

water and biological and pharmaceutical materials and other thermally sensitive materials. In one example, the liquid containing water is contained in a receptacle such as a beaker, Winchester, etc., the device of the invention placed within the liquid and a vacuum applied to the tubular means. The water in the liquid mixture is then drawn through the membrane. The system can be left running until the required degree of dehydration in the liquid mixture is obtained. The device can then be removed, cleaned and used again, or if contaminated e.g. by biological or pharmaceutical material, thrown away.

Thus, an easily transportable device can be obtained for removing water from water containing liquid mixtures, which is adaptable, easy to use and can be employed at the point of use of the liquid mixtures.

It is a feature of the invention that it enables water to be removed from liquid mixtures without the need for high pressure differentials across the membrane as in previously disclosed uses of zeolite membranes.

The invention is described in the Examples and drawing in which the Examples exemplify the preparation of the membrane and the drawing illustrates apparatus for application of the membranes.

Example 1 Membrane Growth

The substrate used was a Pall PSS (Trade Mark) CP 1606 PO5 316L porous sintered stainless steel cylinder filter as illustrated in fig. 1 in which (7) is the cylinder filter and (8) is a screw thread (see Example 3.)

The cylinder was placed in a 1 litre glass vessel which had previously been cleaned by washing with de-ionised water, acetone, toluene and finally acetone before being dried in an oven at 90 degrees C. for 3 hours.

(a) Cobalt pre-treatment:

The cylinder was placed in a 1 litre glass vessel to which was added 800ml of 0.1 M cobalt nitrate solution and left to soak for 1 hour, after which the cobalt nitrate solution was decanted and the beaker was placed in an oven at 90°C to dry, the cylinder was removed from the beaker and fired at 250°C for 4 hours. The cylinder was removed from the furnace and allowed to cool. This procedure was repeated 2 more times to obtain a good cobalt oxide coating.

(b) Zeolite Pre-treatment

Zeolite 4A powder was rubbed into the outside of the substrate, which had already been cobalt coated as above, using a gloved finger, until no more zeolite will rub into the surface, any excess zeolite was tapped off.

Two solutions A and B were prepared separately in two 500 ml glass bottles as follows:-

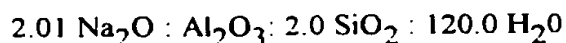
Solution A

73.47g Sodium Aluminate, 11.25g Sodium Hydroxide and 445.8g de-ionised water were mechanically shaken until dissolved. The Sodium Aluminate had an actual composition 62.48% Al_2O_3 , 35.24% Na_2O , and 2.28% H_2O .

Solution B

151.71g Sodium Silicate of composition 14.21% Na_2O , 35.59% SiO_2 and 50.20% H_2O was dissolved in 445.80g de-ionised water.

Solution A was added slowly to solution B with both stirring and shaking by hand to ensure complete and even mixing (it is important that no lumps of hydrogel are formed). This resulted in a hydrogel having a molar composition



800 ml of the hydrogel was slowly poured into a growth vessel containing the cobalt oxide treated and zeolite rubbed cylinder in a vertical position. The growth vessel was placed in a pressure cooker together with a beaker containing the remaining hydrogel solution. The pressure cooker was placed in an oven preheated to 100 degrees C. for 5 hours. Subsequently it was removed from the oven and allowed to cool for 30 minutes. The growth vessel was removed and the solution poured away.

The cylinder was carefully removed from the vessel. The cylinder was placed in a glass vessel and washed three times with 800ml aliquots of de-ionised water, swirling the solution each time to ensure complete removal of residues and the membrane was allowed to air dry in air at 70°C for 2 hours.

The surface of the dried coated cylinder was subsequently wiped clean with a clean lens tissue in order to remove any loose powdery deposits which may have formed on the surface. It was then washed with de-ionised water and left to in an oven at 70°C for 2 hours. This growth and washing process was repeated two more times.

X-ray Analysis showed this to be a Zeolite 4A

Example 2 Preparation of TEOS For Post Treatment of Membrane

The post treatment solution was prepared by placing 120ml of (TEOS) into a clean, dry beaker, adding 540 ml of deionised water and 540ml of ethanol. The mixture was then stirred at 300r.p.m. for a period of 5 mins.

Example 3 Membrane Test Procedure

The cylinder was placed in a 1 litre glass vessel on a heater/stirrer hot plate and a vacuum line was attached to the end of the cylinder by a screw thread. The glass vessel cell was filled with an isopropanol/water (IPA/H₂O) mixture (90/10 wt. % respectively). The membrane was tested at approximately 70°C.

The pressure on the side of the membrane remote from the liquid i.e. inside the cylinder was reduced to 4 mbar (0.4 kN). Permeate was collected over periods of 8 hours and weighed, and small aliquots were analysed, feed water concentration was monitored throughout.

Example 4 Post-treatment Procedure of Membrane

After the initial test of the untreated membrane in the apparatus of Example 3 with IPA/Water, the glass vessel was emptied, rinsed with 2 x 100 ml aliquots of ethanol and then another 100ml aliquot of ethanol was placed into the glass vessel and cylinder was then placed under vacuum for 30 mins.

The ethanol was removed from the glass vessel and the TEOS post-treatment solution prepared as in Example 2 was poured into the glass vessel. The cylinder cell was then treated at 70°C for a period of 24 hours, with the inside of the cylinder under vacuum. After this period, the mix was removed, the heat switched off, vacuum removed and then compressed air was passed over the membrane for a period of one hour.

Example 5

A membrane produced by the method of Example 1 was treated under pervaporation conditions described in Example 3 and the post treatment described in example 4 and the results shown in Table 1 below

Table 1

Isopropanol/Water mixture at 70°C.

Time on Stream (hours)	Feed Water % Weight	Permeate Water % Weight	Permeate Water Flux (J) Kg/m ² /day
0.5	7.99	82.18	27.25
1.0	7.60	80.40	23.26
1.5	7.35	78.14	22.39
2.0	6.45	75.38	21.14
2.5	5.84	72.52	19.79
3.0	5.23	69.45	18.36
3.5	4.88	66.14	18.46
4.0	4.41	60.90	16.14
4.5	3.75	57.61	15.05
5.0	3.46	57.32	13.25
5.5	3.16	48.26	13.18
6.0	2.69	45.93	12.30
6.5	2.19	42.16	8.76
7.0	1.90	38.42	8.27
7.5	1.59	33.15	8.44
8.0	1.47	29.51	7.89
8.5	1.18	26.44	6.98
9.0	1.16	25.77	6.44
9.5	1.00	22.02	5.56
10.0	0.86	21.31	4.87
10.5	0.75	20.34	4.35
11.0	0.66	18.16	3.91
11.5	0.60	16.06	3.26
12.0	0.52	13.98	2.68
12.5	0.44	10.59	1.89

An embodiment of the invention showing equipment in use is shown in fig. 2 in which a receptacle (1) contains a liquid mixture (2) containing water. A tube (3) made of metal mesh has a lower portion (4) on which is deposited a zeolite membrane.

In use the tube is placed in the water-containing liquid in the receptacle and a vacuum is applied at (5). Water is drawn through membrane (4) into the tube, as shown at (6), from where it can be removed. Thus, the liquid (2) left behind, contains a lower proportion of water.

In an alternative application the water containing liquid is placed within the tube (3) and the pressure reduced outside the tube. Water then passes through the membrane leaving a liquid with reduced water content in the tube.

Claims

1. Equipment for separating liquids which comprises a tubular means which is closed at one end and open at the other and in which part of the tube comprises a zeolite membrane.
2. Equipment as claimed in claim 1 in which the tubular means containing a zeolite membrane is a zeolite membrane formed on a supported matrix.
3. Equipment as claimed in claim 2 in which the supported matrix is a metal mesh or sieve or a ceramic or a polymeric material.
4. Equipment as claimed in claim 3 in which the supported matrix is formed into the desired shape and the zeolite membrane crystallised on to the supported matrix.
5. Equipment as claimed in any one of claims 1 to 4 in which the zeolite membrane is treated by being contacted with a silicic acid to form a membrane substantially free of holes.
6. Equipment as claimed in any one of claims 1 to 5 which comprises a substantially cylindrical supported matrix on which is deposited a zeolite membrane so that the zeolite membrane is formed on at least the lower part of the equipment adjacent its closed end.
7. A method of removing water from a liquid mixture which comprises placing equipment as claimed in any one of claims 1 to 6 in contact with the liquid mixture so that substantially the only water permeable part of the equipment in contact with the liquid mixture is that comprising the zeolite membrane, so that water passes through the zeolite membrane and is separated from the liquid mixture.
8. A method as claimed in claim 7 in which the liquid mixture is contained in a vessel.
9. A method as claimed in claim 7. in which the liquid mixture is put inside the equipment so that water passes out through the zeolite membrane.

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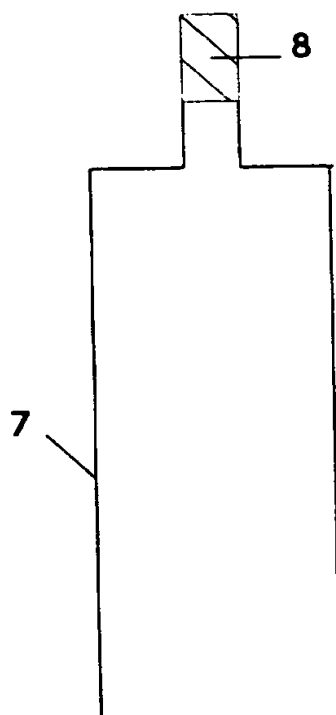


Fig.1

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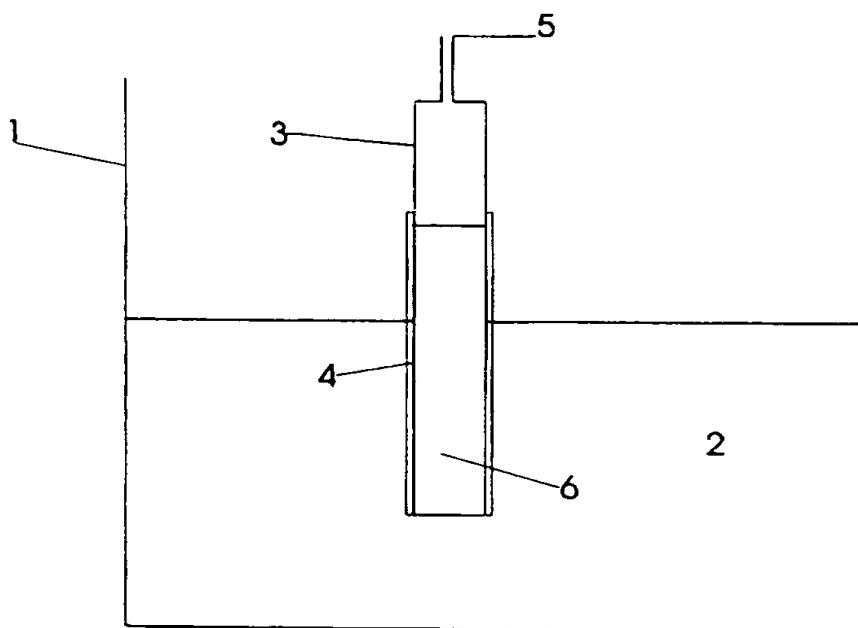


Fig. 2

INTERNATIONAL SEARCH REPORT

Patent Application No. **PCT/GB 96/02861**

A. CLASSIFICATION OF SUBJECT MATTER

B 01 D 63/06, B 01 D 71/02, B 01 D 69/10, B 01 D 67/00,
B 01 D 61/00, B 01 J 29/00, B 01 J 20/18

According to International Patent Classification (IPC) or to both national classification and IPC⁶

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B 01 D, B 01 J, C 02 F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP, A, 0 481 660 (THE BRITISH PETROLEUM COMPANY) 22 April 1992 (22.04.92), claims.	1-4
A	DE, A, 3 827 049 (SCHULTEN) 15 February 1990 (15.02.90), claims.	1-4
A	EP, A, 0 540 485 (AKTIEBOLAGET ELECTROLUX) 05 May 1993 (05.05.93), claims.	1, 7
A	EP, A, 0 659 469 (MITSUI ENGINEERING & SHIPBUILDING) 28 June 1995	1-3

☒ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

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Date of the actual completion of the international search
21 March 1997

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International Application No
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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	(28.06.95), claims. -- US, A, 5 464 798 (SIA) 07 November 1995 (07.11.95), claims. ----	1,2,6

ANHANG

zum internationalen Recherchen-
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ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
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PCT/GB 96/02861 SAE 147977

In diesem Anhang sind die Mitglieder
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This Annex lists the patent family
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In Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
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